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The Effect of Hydrogen on Transport Properties of Highly Permeable Metal Membranes

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1 Introduction

Highly permeable metal membranes for hydrogen separation in fuel cell systems have the potential to reduce system complexity and increase system efficiency. The mechanism of hydrogen permeation leads to almost ideal selectivity of metal membranes. Within this mechanism diffusion of hydrogen through the metal, which is generally considered being Fickian type diffusion, is often regarded to be the limiting step. Under high hydrogen loads this functional representation is not sufficient. Hydrogen interactions within the metal lead to a concentration dependent diffusion coefficient and hydrogen induced stresses have to be taken into account as part of the chemical potential of hydrogen. By permeation experiments with a palladium silver capillary membrane we show the influence of hydrogen on permeation rate and develop a model that fully accounts for the effects mentioned above and explains the unusual permeation characteristic of this membrane.

2 Experimental Procedure

Hydrogen permeation rates through a palladium silver (PdAg) capillary membrane were measured at temperatures between 200 °C and 500 °C. Experiments were carried out using pure (99.999 %) hydrogen. High feed pressures of up to 9 bar were applied on the outside of the membrane. After permeating through the capillary wall hydrogen left only through one end of the capillary at approximately atmospheric pressure. Hydrogen flow was measured with a bubble flow meter. The other end of the capillary was kept closed while the membrane was allowed to expand freely under high hydrogen loads.

3 Experimental Results

As can be seen in Figure 1 permeation rates show a large increase between 200 °C and 250 °C and a strong change in dependence on feed pressure. At temperatures between 300 °C and 380 °C permeation rates do not change within experimental error. At higher temperatures permeation rates show a low increase with increasing temperature.

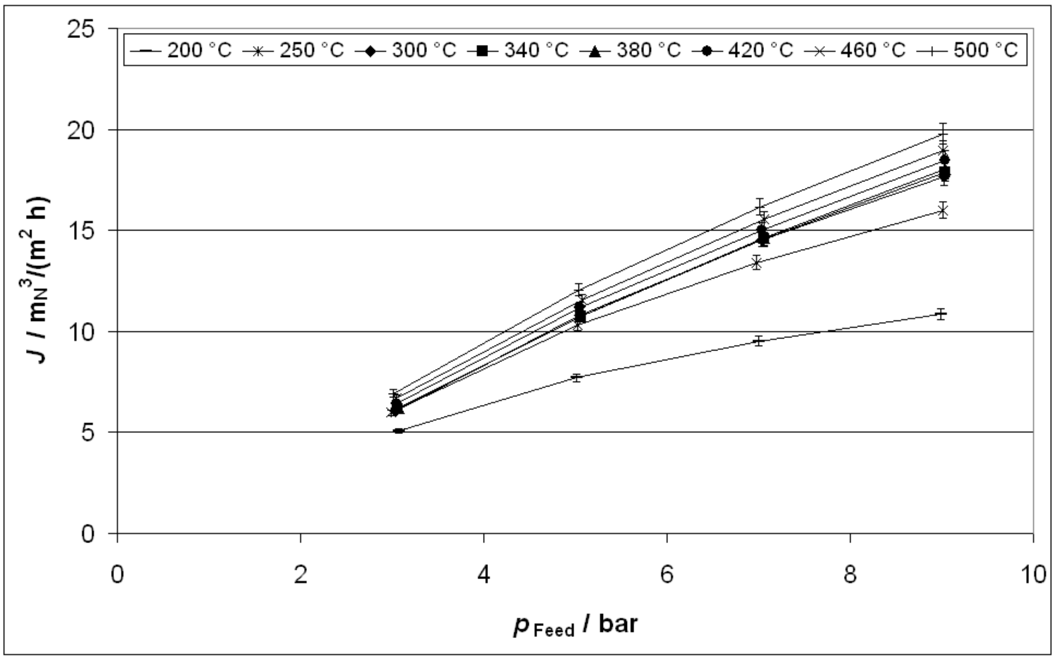

Figure 1: Permeation rates through the capillary PdAg membrane.

4 Model Development

To investigate the cause of this permeation behaviour a permeation model for PdAg was developed based on a well known model by *Ward and Dao* [1] for pure Pd that takes into account all transport steps of the hydrogen permeation mechanism through metals.

Using hydrogen partial pressures on the feed and permeate side and membrane temperatures that were applied during the experiments permeation rates were calculated using the new model. However the results did neither match the experimental values nor could explain the origin of the unusual permeation characteristic. Measured permeation rates were higher than the calculated fluxes up to a temperature of 420 °C. Calculations showed that hydrogen permeation through the capillary should be mainly limited by diffusion through bulk metal above about 250 °C.

The diffusion flux is represented by a Fickian type diffusion equation in the model. But hydrogen diffusion in metals especially under high hydrogen concentrations is more accurately represented by

$$J = -M(c)c\nabla\mu \ , \tag{1}$$

where *M*(*c*) is the mobility of hydrogen atoms which can be related to the macroscopic diffusion coefficient, c is the hydrogen concentration in the metal an μ is the chemical potential of hydrogen in the membrane. To adequately model the diffusion flux of hydrogen through PdAg under high hydrogen concentration the concentration dependent diffusion coefficient (the mobility) of hydrogen must be known as well as the chemical potential gradient in the membrane.

To calculate the diffusion coefficient it has to be taken into account that hydrogen diffusion takes place via activated jumps between interstitial sites. Whether a jump between a starting interstitial site *i* and a target interstitial site *j* takes place is mainly dependent on

- the jump frequency of hydrogen atoms,
- the probability that a hydrogen atom occupies interstitial site *i*,
- the probability that interstitial site *j* is not occupied,
- the probability that *j* is a next neighbour site of *i*,
- the probability that the hydrogen atom is capable of overcoming the activation energy of the jump due to its thermal energy and
- the interaction between hydrogen atoms and between hydrogen atoms and the host metal.

A solubility model of hydrogen in PdAg that is able to cover the thermodynamic aspects of diffusion (site occupancy, interactions) was taken from *Salomons et al.* [2]. A diffusion model for hydrogen in a binary alloy that is compatible to the solubility model was taken from *Brouwer et al.* [3] and modified to describe hydrogen diffusion in face centered cubic binary alloys via octahedral sites, namely palladium silver. It turned out to be essential that hydrogen diffusion through PdAg is mainly governed by jumps through Pd-rich sites as stated by *Züchner et al.* [4]. We found that taking into account only diffusion through octahedral sites with six or five Pd atoms leads to reasonable results which is in agreement with the findings of *Züchner et al.* [4] for a $Pd_{90}Ag_{10}$ alloy.

Values of the diffusion coefficient at negligible hydrogen concentrations depending on the silver concentration in the alloy were calculated and compared to literature data from *Holleck* [5] between 300 °C and 600 °C. The calculated values agree well with the values of *Holleck* [5] up to an Ag concentration of 30 %. At higher silver contents and lower temperatures the modelled values deviate somewhat from the measured values. However since PdAg alloys with Ag contents above 30 % are not regarded to be suitable alloys for membranes used for hydrogen separation the model was considered to be sufficiently accurate.

Additionally concentration profiles in a $Pd_{77}Ag_{23}$ membrane at 150 °C and high hydrogen feed concentrations have been calculated. The profiles show a strong dependence on feed concentration and agree very well with profiles that have been calculated by *Wang et al.* [6].

To include the total influence of the chemical potential gradient of hydrogen in the membrane, the hydrostatic stress gradient has to be taken into account. This gradient is generated by the non-uniform hydrogen induced expansion of the capillary in radial direction due to the concentration gradient in the metal.

The hydrostatic stress component σ_h in a freely expanding cylindrical membrane can be calculated by

$$\sigma_h = -\frac{2}{9}\frac{V_H E\, n}{(1-\nu)}\left(c(r)-\bar{c}\right) \tag{2}$$

where V_H is the partial molar volume of hydrogen in the metal (1,81 x 10^{-6} m^3/mol_H), E is young's modulus (120 GPa), n is the number of metal atoms per volume, ν is the Poisson ratio (0,39), $c(r)$ is the hydrogen concentration in the membrane and $\overline{c}$ is the mean concentration of hydrogen.

5 Discussion of Model Results

To show the influence of high hydrogen concentrations on hydrogen transport through the PdAg capillary permeation rates were calculated using experimental parameters and assuming equilibrium between hydrogen in the gas and in the membrane on the feed and permeate side. For temperatures of 200 C and 250 °C these permeation rates exceed experimental values by about 30 %, however show a similar increase with temperature and a similar change in pressure dependence. It can be assumed that this deviation exists because the assumption of linear elastic material behaviour does not apply under high hydrogen concentration and stresses that presumably existed in the metal. For temperatures between 300 °C and 500 °C relative deviations of the calculated permeation rates from the experimental values are shown in Figure 2. The dashed lines represent the experimental error.

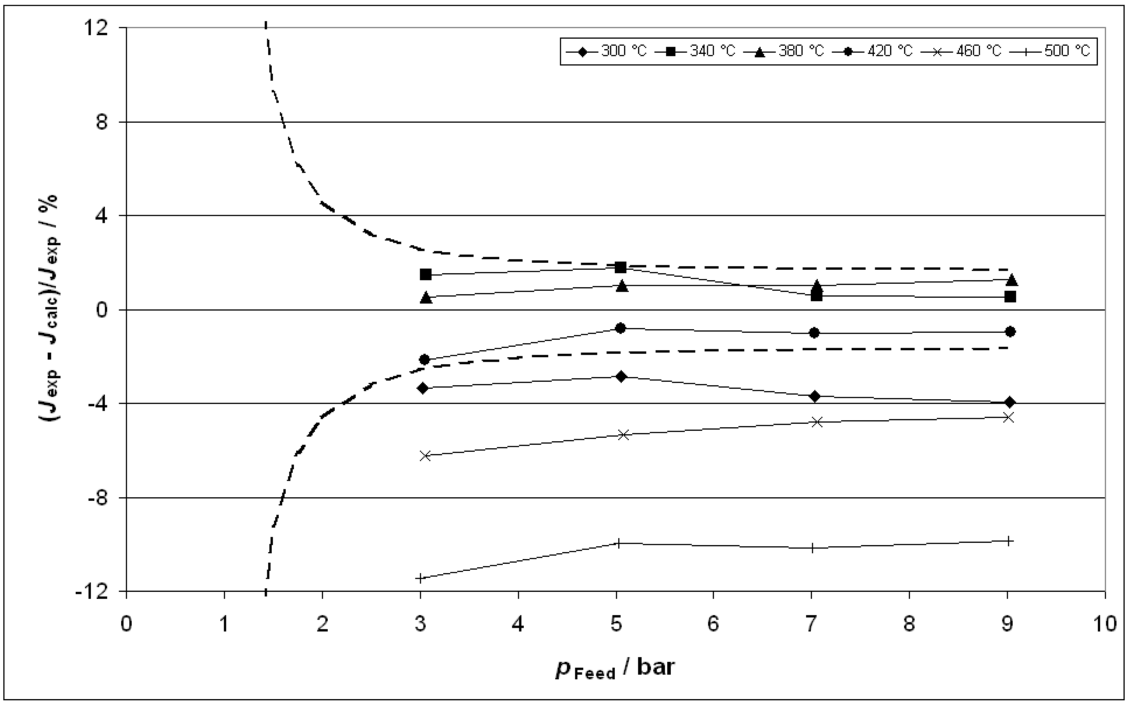

Figure 2: Relative deviations of measured and modelled permeation rates between 300 °C and 500 °C.

It can be seen that between 340 °C and 420 °C the model values coincide with the experimental values within the experimental error. At 300 °C the measured permeation rates are about 4 % lower than the calculated values. Above 420 °C the increase of modelled permeation rates tends to be higher than the increase of the measured ones, which is probably caused by an over-prediction of hydrogen concentrations in the metal by the solubility model of *Salomons et al*. [2]. No parameters were used to fit modeling data to experimental results.

For a hydrogen partial feed pressure of 9 bar hydrostatic stresses in the capillary were calculated. On the feed side the metal is under compressible stresses between about –600 MPa and –200 MPa. Calculated hydrostatic tensile stresses on the permeate side reach as high as 800 MPa at 250 °C. These large tensile stresses probably exceed the yield stress of the metal. Further investigation is needed to explain why the membrane was not severely damaged under these conditions.

Although hydrogen solubility at 200 °C is higher than at 250 °C maximum stresses occur at 250 °C due to an increasing overall concentration gradient in the membrane between 200 °C and 250 °C that also causes the large increase of permeation rates in this temperature range.

6 Conclusions

A freely expanding capillary membrane shows unusual permeation behaviour between 200 °C and 500 °C at elevated hydrogen partial feed pressures up to 9 bar. To explain this permeation behaviour a detailed permeation model was set up that fully accounts for all transport steps of the hydrogen permeation mechanism through metals. Calculations with this model show that permeation through the capillary was limited by diffusion, however fails to explain the permeation characteristic. By developing a model for the concentration dependent diffusion coefficient of hydrogen through PdAg and taking into account the effect of hydrostatic stress gradient on permeation the permeation model was improved. Calculations show that the unusual permeation characteristic of the capillary can be explained by hydrogen interactions within the metal and the stress gradient generated by hydrogen induced expansion of the metal. The gradient of hydrostatic stress improves hydrogen permeation in freely expanding cylindrical membranes. The permeation model can also be used to predict hydrogen induced stresses in PdAg.

References

[1] *Ward, T and Dao, T*: Model of hydrogen permeation behaviour in palladium membranes. Journal of Membrane Science, 153, 1999, 211-231

[2] *Salomons, E, Hemmes, H and Griessen, R*: Hydrogen spectroscopy of $Pd_{1-y}Ag_y$ and $Pd_{1-y}Cu_y$ alloys. Journal of Physics: Condensed Matter, 2, 1990, 817-834

[3] *Brouwer, R, Salomons, E and Griessen, R*: Diffusion of hydrogen in Nb1-yVy alloys. Physical Review B, 38 (5), 1988, 10217-10226

[4] *Züchner, H, Barlag, H and Majer, G*: The existence of more than one jump process of hydrogen in palladium-silver alloys – an NMR study. Journal of Alloys and Compounds, 330-332, 2002, 448-453

[5] *Holleck, G*: Diffusion and solubility of hydrogen in palladium and palladium-silver alloys. The Journal of Physical Chemistry, 74 (3), 1970, 503-511

[6] *Wang, D, Flanagan, T and Shanahan, K*: Diffusion of H through Pd-Ag alloys (423 – 523 K). Journal of Physical Chemistry B, 112, 2008, 1135-1148